(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 310 248 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 88308081.4

(22) Date of filing: 01.09.88

(51) Int. Cl.4: H01L 39/24 , H01J 37/30 , G03G 5/02

(30) Priority: 08.12.87 US 130135
30.09.87 US 103245

(43) Date of publication of application: 05.04.89 Bulletin 89/14

(84) Designated Contracting States: DE FR GB

(71) Applicant: GENERAL MOTORS CORPORATION
General Motors Building 3044 West Grand Boulevard
Detroit Michigan 48202(US)

(72) Inventor: Mantese, Joseph Vito
61331 Windwood Ct.
Washington Michigan 48094(US)
Inventor: Micheli, Adolph Louis
38900 Elmite
Mt. Clemens Michigan 48045(US)
Inventor: Hamdi, Aboud Halal
3988 Dorothy St.
Detroit Michigan 48211(US)
Inventor: Catalan, Antonio Buddy
3658 Merrimac
Sterling Heights Michigan 48077(US)

(74) Representative: Haines, Arthur Donald et al
Patent Section (F6) Vauxhall Motors Limited
P.O. Box 3 Kimpton Road
Luton, Beds. LU2 OSY(GB)

(54) Patterning thin film superconductors using focused beam techniques.

(57) Patterned films of superconducting materials are formed using focused beam techniques, such as electron beam, ion beam, and laser beam techniques. A solution comprising the neodecanoates of yttrium, barium, and copper is formed which is soluble in an organic solvent. The solution is spun onto an appropriate substrate. The solution is dried and subsequently selectively exposed using focused beam techniques, so that the exposed regions are no longer soluble in the organic solvent. The dried solution is immersed in the organic solvent, so that the only the exposed, insoluble regions remain on the substrate. The dried solution is then heated at a temperature sufficient to decompose the neodecanoates, about 450°C, and then heated again to promote recrystallizaton and grain growth of the remaining metal oxides. The resulting patterned film exhibits superconductive characteristics.

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PATTERNING THIN FILM SUPERCONDUCTORS USING FOCUSED BEAM TECHNIQUES

This invention relates to superconducting materials. More particularly, this invention relates to methods for patterning films of superconducting materials as specified in the preamble of claim 1, for example as disclosed in the article entitled "Metal deposition by electron beam exposure of an organometallic film" by Craighead and Schiavone, published in Appl. Phys. Lett. 48 (25) on 23 June 1986.

Background of the Invention

Films of superconducting materials have been formed using metallo-organic deposition techniques. Superconducting films formed by metallo-organic deposition offer many advantages over standard methods for film preparation and deposition. A significant advantage is that the metallo-organic deposition process does not require vacuum processing. In addition, the chemical constituents of the films may be altered with ease.

Examples of such superconducting materials prepared using metallo-organic deposition techniques, are disclosed in our co-pending patent application in Europe Serial No. , filed on the same date, and herein incorporated by reference.

Metallo-organic deposition of the thin film superconductors generally involves a three-step process. First, an organic liquid, such as the composition comprising yttrium, barium, and copper neodecanoates disclosed in the aforesaid patent application in Europe, is spin-coated onto a suitable substrate. The organic film is then cured in air at about 500 °C for about five minutes. Finally, the organic film is baked in an oxygen-containing atmosphere for about six hours at about 850 °C, and slow-cooled to room temperature. The resulting empirical composition for the superconducting thin films prepared in accordance with the metallo-organic deposition techniques is $Y_1Ba_2Cu_4O_z$, with z ranging between about 6-8. Electrical measurements indicate a superconducting transition temperature of about 90 °K for these superconducting materials, with the temperature of zero state resistance as high as about 70 °K.

It is desirable to provide a method for patterning films of superconducting material.

Summary of the Invention

A method for producing patterned films of superconductor materials according to the present invention is characterised by the features specified in the characterising portion of claim 1.

It is an object of the present invention to provide patterned films of superconductor material.

It is a further object of this invention to provide a method for forming patterned films of superconductor material.

It is still a further object of this invention that these patterned superconductor films be formed using focused beam techniques.

In accordance with a preferred embodiment of this invention, these and other objects and advantages are accomplished as follows.

For the first time a method is disclosed for forming patterned superconductor films by patterning metal neodecanoate organic films, which subsequently are reduced to superconducting films of YBaCuO, and exposing the neodecanoates contained within the metallo-organic films to focused beams of radiation.

Initially a yttrium, barium, copper neodecanoate solution is spin-coated onto a suitable substrate, much like conventional photo-resist liquid is spun onto a silicon wafer. The solvent within the neodecanoate solution is driven off from the organic film by pre-baking the film and substrate at a temperature below the decomposition temperature for the metal neodecanoates, about 25-450 °C, for a short period of time, of about five minutes. The metal neodecanoate organic film is still soluble in a xylene-pyridine solvent solution after this pre-baking step. The pre-baked metal neodecanoate organic film is then patterned, by exposing selected areas of the organic film to focused beams of radiation such as electrons, ions, or laser light. This exposure renders the metal neodecanoate material insoluble in the xylene-pyridine mixture where the focused beams of radiation have impinged upon the organic film.

The pre-baked organic film and substrate is then rinsed in the xylene-pyridine solution which acts as a developer to remove the unexposed regions of the organic film, so that only the portions of the metal neodecanoate film which have been exposed to the focused beams remain on the substrate. The substrate and patterned metallo-organic film is then fully cured at 500 °C for about five minutes, so as to fully decompose the metal neodecanoates and leave only the corresponding metal oxides on the substrate surface. The cured metal oxide film is subsequently annealed in an oxygen atmosphere at about 850-1000 °C for a period of time up to about 60 minutes, cooled to about 200 °C, and rapid quenched to room temperature. The resulting patterned material is superconductive.

Other objects and advantages of this invention will be better appreciated from a detailed description thereof, which follows.

Detailed Description of the Invention

In the present invention, organic inks are prepared using the neodecanoates of yttrium, barium, and copper. Yttrium and barium neodecanoates were formed from their metal acetates by reaction with ammonium neodecanoate. The copper neodecanoate was formed by a reaction of copper-(II) acetate with tetramethyl ammonium neodecanoate. Several solutions containing the three neodecanoates, of various concentrations, were made by dissolving the three components in a solvent containing appropriate amounts of xylene and pyridine.

The solution, i.e., ink, which resulted in the preferred superconductor film composition of $YBa_2Cu_4O_z$ has a ratio of one gram of the combined metal neodecanoates to one millilitre of solvent. 8.54 grams of yttrium neodecanoate, 19.12 grams of barium neodecanoate, and 13.76 grams of copper neodecanoate, yielding a total of 41.42 grams of metal neodecanoate, were dissolved in 41.42 millilitres of solvent, the solvent comprising 39.35 millilitres of xylene with 2.07 millilitres of pyridine. The usual solvent for the metal neodecanoates is pure xylene, however, it was observed that the yttrium neodecanoate gels in xylene, forming an unusable ink. Therefore, the addition of approximately five volume percent pyridine to the xylene forms a solvent that will not gel the yttrium neodecanoate. The solutions were filtered to remove particles down to approximately 200 nanometres size.

The inks prepared from the metal neodecanoates and solvents were flooded onto single crystal strontium titanate, $SrTiO_3$, substrates, oriented in the <l00>crystal direction. The inks were spun dry on the substrates at various speeds, about 2000 revolutions per minute for about 20 seconds being preferred, although suitable results have been obtained using 1000-10000 revolutions per minute.

The xylene-pyridine solvent within the metal neodecanoate solution is driven off from the metal neodecanoate organic film by pre-baking the film and substrate in air at a temperature less than the decomposition temperature for the metal neodecanoates, i.e., about 25-450° C, for a short period of time, preferably at a temperature of about 110° C for about five minutes. At this point, after the pre-baking step at a temperature less than the metal neodecanoate decomposition temperature, the organic neodecanoate film is still soluble in a xylene-pyridine solvent solution. The pre-baked organic neodecanoate film is then patterned, by exposing selected areas of the organic film to focused beams of electrons, ions, or laser light. This exposure renders the material insoluble in the xylene-pyridine mixture where the focused beams have impinged upon the organic film.

The three focused beam techniques employed to form the patterned superconductor films are, respectively, electron beam, ion beam, and laser beam techniques. Using electron beam techniques, selected areas of the pre-baked metal neodecanoate organic films are exposed to an electron beam having an energy ranging between about 20-50 keV. The diameter of the focused beam may vary between about 5-500 nanometres, therefore resulting in superconducting patterns of various dimensions.

The electron beam renders the exposed regions of the metal neodecanoate organic film insoluble in the xylene-pyridine solvent solution. The pre-baked substrate and metal neodecanoate organic film, which has been selectively exposed to the focused electron beam, are then rinsed in the xylene-pyridine solution.

The xylene-pyridine solvent solution acts in an analogous manner to that of a photographic fixer solution, so as to remove the unexposed regions of the organic film. Therefore, only the selectively-exposed portions of the metal neodecanoate organic film remain on the substrate.

The patterned metallo-organic film is then fully cured at about 500° C for about five minutes, so as to fully decompose the metal neodecanoates and leave only the metal oxides on the substrate surface. Complete decomposition of the combined neodecanoates occurs at about 450° C. The cured metal oxide film is subsequently annealed in an oxygen atmosphere at about 850-1000° C for a duration ranging up to to about 60 minutes, to promote recrystallization and grain growth. The film is cooled to about 200° C and rapid-quenched to room temperature. The first cooling step to about 200° C may range between either substantially instantaneously, i.e., quenched, or a slow cooling rate, i.e., about 100° C per hour, as no particular rate of cooling is preferred. The resulting patterned material is superconductive and has a preferred relative metal composition of $YBa_2Cu_4O_z$, with z ranging between about 6-8.

The pre-baked metal-neodecanoate organic films may also be patterned using ion beam methods. The focused ion beam generally requires shorter exposure times and lower ion dosages, as compared to exposing the material using focused electron beam methods, because the ions have a greater mass than the electrons, and therefore impart more energy. After the metal neodecanoate organic films have been pre-baked, so as to drive off the organic xylene-pyridine solvent present in the films, the films may be patterned using a focused ion beam.

Generally, any ion-forming element may be used to form the focused ion beam, so as to pattern the metal neodecanoate organic films. However, the preferred focused ion beams for patterning these metal neodecanoate films are gallium (Ga^+), boron (B^+ or B^{++}), oxygen (O^+ or O^{++}), phosphorus (P^+ or P^{++}), or silicon (Si^+ or Si^{++}). The preferred patterning results are obtained for these various materials, using an ion beam energy of about 10-400 keV, a dosage of about 10^{13} - 10^{16} ions per square centimetre, and a focused beam diameter of about 5-500 nanometres. The metal neodecanoate material which has been exposed to the focused ion beams is rendered insoluble in xylene-pyridine solvent solution. Thus the ion beam method renders those selective areas that have been exposed to the focused ion beam insoluble in the xylene pyridine solvent subsequently applied to the exposed films. Therefore, similarly to the electron beam method disclosed above, only those areas which have not been exposed to the focused beam remain soluble in the xylene-pyridine solvent.

After the metal neodecanoate films have been exposed to the focused ion beam, the substrate and films are rinsed in the xylene-pyridine solvent solution which acts in the same manner as a photographic fixer solution to remove the unexposed regions of the organic film. After rinsing in the xylene-pyridine solvent solution, only the selectively-exposed portions of the organic neodecanoate films remain on the substrate. The patterned metal neodecanoate organic films on the substrate are then fully cured at 500°C for about five minutes, so as to fully decompose the metal neodecanoates. Complete decomposition of the metal neodecanoates occurs at about 450°C. Therefore only the metal oxides remain on the substrate surface after the curing step. The cured metal oxide films are subsequently annealed in an oxygen atmosphere at about 850-1000°C for a duration ranging up to about 60 minutes. The films are then cooled to about 200°C, and rapid-quenched to room temperature. The cooling step to 200°C may vary between instantaneous cooling i.e., quenching, or slow cooling, i.e., about 100°C per hour, as no particular rate is preferred. The resulting patterned films are superconductive and have a preferred relative metal composition of $YBa_2Cu_4O_z$, with z ranging between about 6-8.

The third method which is disclosed for forming patterned superconductive films involves laser beam techniques. The pre-baked metal neodecanoate organic films, which have been spun-on to the appropriate substrate, such as strontium titanate, are patterned using laser beam methods. The focused laser beam exposes selective regions of the metal neodecanoate films, by imparting heat to the selected regions of the material and rendering that material insoluble in xylene-pyridine solvent solution. An advantage of the laser beam method is that the focused laser beam may locally heat the desired areas above the metal neodecanoate decomposition temperature of about 450°C, therefore eliminating the curing step after patterning required with the electron beam or ion beam methods hereinbefore disclosed.

After the metal neodecanoate organic films have been pre-baked at a temperature less than the metal neodecanoate decomposition temperature, so as to drive off the organic xylene-pyridine solvent present therein, the films are patterned by exposing the selected areas of the film to a focused laser beam. Preferably, the focused laser beam has a beam diameter of about 100-1000 nanometres and a beam energy of about 0.1-100 Watts. Generally, the wavelength of the laser beam does not significantly affect the results of the exposure. The focused laser beam renders those selective areas that have been exposed to the focused laser beam insoluble in xylene-pyridine solvent solution. Further, depending on the parameters of the laser beam employed, those selected areas will also be locally cured if the laser beam imparts enough localized heat to raise the temperature of the films above the metal neodecanoate decomposition temperature of about 450°C. This eliminates the need for the subsequent curing step, which is necessary for the electron beam and ion beam methods.

After the metal neodecanoate films have been exposed to the focused laser beam, the substrate and films are rinsed in the xylene-pyridine solvent solution which acts in the same manner as a photographic fixer solution to remove the unexposed regions of the organic films. The rinsing step occurs regardless of whether the exposed areas had been heated above the metal neodecanoate decomposition temperature. After rinsing in the xylene-pyridine solvent solution, only the selectively exposed, insoluble portions of the organic neodecanoate films remain on the substrate. The substrate and patterned metal neodecanoate organic films are fully cured at 500°C for about five minutes, so as to fully decompose the metal neodecanoates. The curing step is optional depending on whether the focused laser beam parameters are such that complete decomposition of the metal neodecanoates will occur. After decomposition of the metal neodecanoates, whether by the focused laser beam or subsequent curing step, only the metal oxides remain on the substrate surface. The cured metal oxide films are subsequently annealed in an oxygen atmosphere at about 850-1000 °C for a duration ranging up to about 60 minutes, so as to promote recrystallization and grain growth. This is followed by cooling the films to about 200 °C, the cooling rate being between instantaneous quenching to a very slow cooling rate of about 100 °C per hour. The films are then rapid-quenched to room temperature. The resulting patterned film is superconductive and has a preferred relative metal composition of $YBa_2Cu_4O_z$, with z ranging between about 6-8.

With this invention, superconducting thin films of various compositions may be formed. This invention readily facilitates modification of the focused beam parameters, metal constituents, and their ratios within the thin films, and patterned configurations, to obtain optimal superconducting film characteristics.

Claims

1. A method for producing patterned films of superconductor materials by the irradiation of a metallo-organic film deposited on a substrate to expose selected regions of said film in a predefined pattern, followed by the removal of unexposed regions of said film with the use of a solvent, characterised in that the method comprises the steps of: forming a solution from the neodecanoates of metals, which metals can form an oxide mixture exhibiting superconductive properties, said solution being soluble in an organic solvent; depositing as said metallo-organic film a film of said solution onto said substrate; exposing said selected regions of said film to radiation so that said exposed selected regions of said film become insoluble in said organic solvent; immersing said film into said organic solvent so that said removal of unexposed regions of said film with said organic solvent allows said insoluble, exposed regions of said film to remain on said substrate; heating said film at a first temperature for a period of time that is (a) sufficient to thermally decompose said metal neodecanoates in said insoluble, exposed regions of said film into the corresponding metal oxides, and (b) insufficient to significantly recrystallize said metal oxides; and heating said metal oxide exposed regions at a second temperature for a period of time that is sufficient to promote recrystallization and grain growth of said metal oxides within said exposed regions and to induce a change therein by which said exposed regions of said film exhibit superconducting properties.

2. A method for producing patterned films of superconductor materials according to claim 1, characterised in that said film is exposed to radiation in the form of a focused beam of radiation.

3. A method for producing patterned films of superconductor materials according to claim 2, characterised in that the focused beam of radiation is an electron beam.

4. A method for producing patterned films of superconductor material according to claim 3, characterised in that said focused electron beam has a beam diameter ranging between about 5 to about 500 nanometres, and has an energy level ranging between about 20 to about 50 keV.

5. A method for producing patterned films of superconductor materials according to claim 2, characterised in that the focused beam of radiation is an ion beam.

6. A method for producing patterned films of superconductor material according to claim 5, characterised in that the ion beam is formed from ions of gallium, boron, oxygen, phosphorus, or silicon.

7. A method for producing patterned films of superconductor material according to claim 5 or 6, characterised in that said focused ion beam has a beam diameter ranging between about 5 to about 500 nanometres, an energy level ranging between about 10 to about 400 keV, and produces an ion dosage ranging between about 10^{13} to about 10^{16} ions per square centimetre.

8. A method for producing patterned films of superconductor materials according to claim 2, characterised in that the focused beam of radiation is a laser beam.

9. A method for producing patterned films of superconductor material according to claim 8, characterised in that said focused laser beam has a beam diameter ranging between about 100 to about 1000 nanometres, and said laser beam has an energy level ranging between about 0.1 to about 100 Watts.

10. A method for producing patterned films of superconductor materials according to any one of the preceding claims, characterised in that said solution contains the metal neodecanoates of yttrium, barium, and copper.

11. A method for producing patterned films of superconductor material according to any one of the preceding claims, characterised in that said organic solvent comprises a mixture of xylene and pyridine.

12. A method for producing patterned films of superconductor materials according to any one of the preceding claims, characterised in that the first temperature at which the film is heated is greater

than 450 °C, and the second temperature at which the film is heated ranges between about 850 °C to about 1000 °C.

13. A patterned film of superconductor material produced in accordance with any one of the methods of the preceding claims.